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Signed this 31st day of August 2007

C. E. SITCH
Managing Director - UK Translation Division
For and on behalf of RWS Group Ltd

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DATE OF FILING ASSIGNED BY THE INPI 23 OCT. 2002

1 NAME AND ADDRESS OF THE APPLICANT OR THE REPRESENTATIVE TO WHOM THE CORRESPONDENCE IS TO BE ADDRESSED

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Your file references:
(optional) OA02334/FA

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2 NATURE OF THE APPLICATION	**Tick one of the 4 following boxes**
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3 **TITLE OF THE INVENTION** (200 characters or spaces maximum)

Oil-in-water oxidizing cream emulsion for treating human keratin fibres

4 **PRIORITY DECLARATION OR APPLICATION FOR THE BENEFIT OF THE FILING DATE OF A PRIOR FRENCH APPLICATION**	Country or organisation Date ___/___/___ No. Country or organisation Date ___/___/___ No. Country or organisation Date ___/___/___ No. ☐ **If there are other priorities, tick the box and use the "continuation" form**
5 **APPLICANT**	☐ **If there are other applicants, tick the box and use the "continuation" form**
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The inventors are the applicants		☐ Yes ☒ No **In this case, provide a separate designation of the inventor(s)**
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10 SIGNATURE OF THE APPLICANT OR REPRESENTATIVE (name and capacity of the signatory)

Catherine WATTREMEZ
[signature]
23 October 2002

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L. MARIELLO

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OIL-IN-WATER OXIDIZING CREAM EMULSION FOR TREATING HUMAN KERATIN FIBRES

The present patent application relates to an oxidizing cream emulsion for treating human keratin fibres and more particularly the hair, comprising at least one oxidizing agent, at least one (C_8-C_{30}) fatty alcohol, at least one nonionic and/or anionic surfactant and at least one amphiphilic polymer comprising at least one 2-acrylamido-2-methylpropanesulfonic acid unit in free form or partially or totally neutralized form and at least one hydrophobic unit containing from 6 to 50 carbon atoms.

The patent application also relates to the use of the said amphiphilic polymer to stabilize the viscosity of an oxidizing oil-in-water emulsion comprising at least one (C_8-C_{30}) fatty alcohol and at least one nonionic and/or anionic surfactant.

The patent application also relates to dyeing, bleaching and permanent-reshaping processes using the said emulsion.

In cosmetics, in the fields of dyeing, bleaching and permanent-reshaping of human keratin fibres and more particularly of hair, oxidizing compositions are used.

Thus, in the oxidation dyeing of the hair, oxidizing compositions are mixed with oxidation dyes (bases and couplers), which are colourless in themselves, to generate coloured compounds and dyes by a process of oxidative condensation. Oxidizing compositions are also used in the direct dyeing of the hair as a mixture with certain direct dyes that are coloured and colouring, in order to obtain a coloration with a lightening effect on the hair. Among the oxidizing agents conventionally used for dyeing keratin fibres, mention may be made of hydrogen peroxide or compounds capable of producing hydrogen peroxide by hydrolysis, such as urea peroxide, and persalts such

as perborates and persulfates, hydrogen peroxide being more particularly preferred.

In hair bleaching, bleaching compositions contain one or more oxidizing agents. Among these oxidizing agents, the ones most conventionally used are hydrogen peroxide or compounds capable of producing hydrogen peroxide by hydrolysis, such as urea peroxide or persalts such as perborates, percarbonates and persulfates, hydrogen peroxide and persulfates being particularly preferred.

These compositions are mainly formed from anhydrous products that contain alkaline compounds (amines and alkaline silicates), and a peroxygenated reagent such as ammonium or alkali metal persulfates, perborates or percarbonates, which is diluted at the time of use with an aqueous hydrogen peroxide composition.

Bleaching compositions are also in the form of ready-to-use oil-in-water emulsions based on hydrogen peroxide.

For the purposes of the invention, the expression "ready-to-use composition" means the composition intended to be applied in unmodified form to the keratin fibres, i.e. it may be stored in unmodified form before use or may result from the extemporaneous mixing of two or more compositions.

In the permanent reshaping of the hair, in a first stage, the keratin -S-S- disulfide (cystine) bonds are opened using a composition containing a suitable reducing agent (reduction step), followed, after having rinsed the head of hair thus treated, by reconstituting the said disulfide bonds in a second stage, by applying to the hair, which has been placed under tension beforehand (curlers and the like), an oxidizing composition (oxidation step, also known as the fixing step) so as to finally give the hair the desired shape. This technique thus makes it possible either to make the hair wavy or to relax or straighten it. The new shape given to the hair by a chemical treatment

such as above is remarkably long-lasting and especially withstands the action of washing with water or shampoos, as opposed to simple standard techniques of temporary reshaping, such as hairsetting.

The oxidizing compositions required to perform the fixing step are usually compositions based on aqueous hydrogen peroxide solution.

In these cosmetic applications, the oxidizing compositions are usually formulated in the form of oil-in-water (O/W) emulsions based on fatty alcohol and nonionic or anionic surfactant, so as to optimize the application and use qualities of the dyeing, bleaching or permanent-reshaping compositions comprising them, and especially in order for them to have a sufficient consistency so as not to run outside the zones of the head of hair or locks of hair to be treated.

It has been found, however, that the oxidizing O/W emulsions formed from fatty alcohol(s) and from nonionic or anionic surfactant(s) undergo substantial texture and viscosity changes over time, and that the cosmetic compositions formed therefrom lose their usual use qualities. For example, such compositions may thicken substantially over time, thus gradually making it very difficult for hairstylists to extract them from the device containing them.

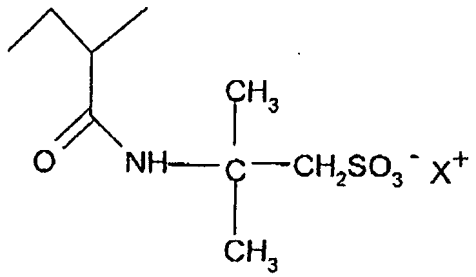
The Applicant has discovered, surprisingly, that it is possible to obtain oxidizing cream O/W emulsions whose viscosity and texture change significantly less over time, if an amphiphilic polymer comprising at least one 2-acrylamido-2-methylpropanesulfonic (AMPS) acid unit in free form or partially or totally neutralized form and at least one hydrophobic unit containing from 6 to 50 carbon atoms are introduced into the oxidizing O/W emulsion.

Thus, the dyeing, bleaching or permanent-reshaping compositions

comprising them are stable and have improved and more efficient application and use qualities.

This discovery forms the basis of the present invention.

One subject of the present invention is thus an oxidizing cream oil-in-water emulsion for treating keratin materials, characterized in that it comprises at least one oxidizing agent, at least one (C_8-C_{30}) fatty alcohol, at least one nonionic and/or anionic surfactant and at least one amphiphilic polymer comprising at least one 2-acrylamido-2-methylpropanesulfonic acid unit in free form or partially or totally neutralized form of formula (I) below and at least one hydrophobic unit containing from 6 to 50 carbon atoms,



(I)

in which X^+ is a proton, an alkali metal cation, an alkaline-earth metal cation or an ammonium ion.

The invention also relates to the use of the said polymer to stabilize the viscosity of an oxidizing O/W emulsion comprising at least one fatty alcohol and at least one nonionic and/or anionic surfactant.

However, other characteristics, aspects, subjects and advantages of the invention will emerge even more clearly on reading the description and the examples that follow.

Amphiphilic polymers comprising at least one 2-acrylamido-2-methylpropanesulfonic

(AMPS) acid unit in free form or partially or totally neutralized form and at least one hydrophobic unit containing from 6 to 50 carbon atoms

The term "amphiphilic polymer" means any polymer comprising both a hydrophilic portion and a hydrophobic portion and especially a fatty chain.

The hydrophobic portion present in the polymers of the invention preferably contains from 12 to 22 carbon atoms.

The amphiphilic polymers in accordance with the invention generally have a number-average molecular weight ranging from 1 000 to 20 000 000 g/mol, preferably ranging from 20 000 to 5 000 000 and even more preferably from 100 000 to 1 500 000 g/mol.

The amphiphilic polymers according to the invention may be crosslinked or non-crosslinked. Crosslinked amphiphilic polymers are preferably chosen.

When they are crosslinked, the crosslinking agents may be chosen from the polyolefinically unsaturated compounds commonly used for crosslinking polymers obtained by free-radical polymerization.

Examples that may be mentioned include divinylbenzene, diallyl ether, dipropylene glycol diallyl ether, polyglycol diallyl ethers, triethylene glycol divinyl ether, hydroquinone diallyl ether, ethylene glycol di(meth)acrylate or tetraethylene glycol di(meth)acrylate, trimethylolpropane triacrylate, methylenebisacrylamide, methylenebis-methacrylamide, triallylamine, triallyl cyanurate, diallyl maleate, tetraallylethylenediamine, tetraallyloxyethane, trimethylolpropane diallyl ether, allyl (meth)acrylate, allylic ethers of alcohols of the sugar series, or other allyl or vinyl ethers of polyfunctional alcohols, and also allylic esters of phosphoric and/or vinylphosphonic acid derivatives, or mixtures of these compounds.

Methylenebisacrylamide, allyl methacrylate or trimethylolpropane triacrylate (TMPTA) will be used more particularly. The degree of crosslinking will generally range from 0.01 mol% to 10 mol% and more particularly from 0.2 mol% to 2 mol% relative to the polymer.

The amphiphilic polymers in accordance with the invention may be chosen especially from random amphiphilic AMPS polymers modified by reaction with a C_6-C_{22} n-monoalkylamine or di-n-alkylamine, such as those described in patent application WO 00/31154. These polymers may also contain other hydrophilic units chosen, for example, from (meth)acrylic acids, β-substituted alkyl derivatives thereof or esters thereof obtained with monoalcohols or mono- or polyalkylene glycols, (meth)acrylamides, vinylpyrrolidone, maleic anhydride, itaconic acid or maleic acid, or mixtures of these compounds.

These same copolymers may also contain one or more units not comprising a fatty chain, such as (meth)acrylic acids, β-substituted alkyl derivatives thereof or esters thereof obtained with monoalcohols or mono- or polyalkylene glycols, (meth)acrylamides, vinylpyrrolidone, maleic anhydride, itaconic acid or maleic acid, or mixtures of these compounds.

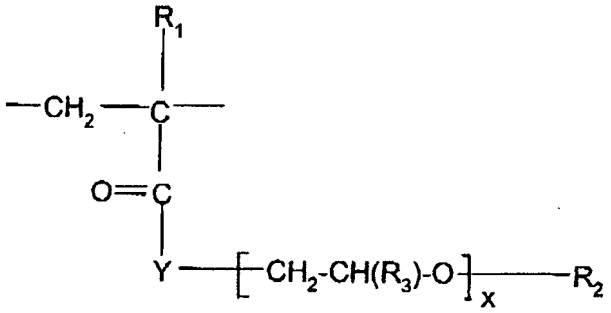
These copolymers are described especially in patent application EP-A-750 899, patent US 5 089 578 and in the following publications from Yotaro Morishima:

- "Self-assembling amphiphilic polyelectrolytes and their nanostructures - Chinese Journal of Polymer Science Vol. 18, No. 40, (2000), 323-336";
- "Micelle formation of random copolymers of sodium 2-(acrylamido)-2-methylpropanesulfonate and a nonionic surfactant macromonomer in water as studied by fluorescence and dynamic light scattering - Macromolecules 2000,

Vol. 33, No. 10 - 3694-3704";

- "Solution properties of micelle networks formed by nonionic moieties covalently bound to a polyelectrolyte: salt effects on rheological behaviour - Langmuir, 2000, Vol. 16, No. 12, 5324-5332";
- "Stimuli responsive amphiphilic copolymers of sodium 2-(acrylamido)-2-methylpropanesulfonate and associative macromonomers - Polym. Preprint, Div. Polym. Chem. 1999, 40(2), 220-221".

The hydrophobic units of these particular copolymers are preferably chosen from the acrylates or acrylamides of formula (II) below:



(II)

in which R_1 and R_3, which may be identical or different, denote a hydrogen atom or a linear or branched C_1-C_6 alkyl radical (preferably methyl); Y denotes O or NH; R_2 denotes a hydrophobic hydrocarbon-based radical containing from 6 to 50 carbon atoms and more preferably from 12 to 22 carbon atoms; x denotes a number of moles of alkylene oxide and ranges from 0 to 100.

The radical R_2 is preferably chosen from linear C_6-C_{18} alkyl radicals (for example n-hexyl, n-octyl, n-decyl, n-hexadecyl and n-dodecyl) and branched or cyclic C_6-C_{18} alkyl radicals (for example cyclododecane (C_{12}) or adamantane (C_{10})); C_6-C_{18} perfluoroalkyl radicals (for example the group of formula $-(CH_2)_2-(CF_2)_9-CF_3$); the

cholesteryl radical (C_{27}) or a cholesterol ester residue, for instance the cholesteryl oxyhexanoate group; aromatic polycyclic groups, for instance naphthalene or pyrene.

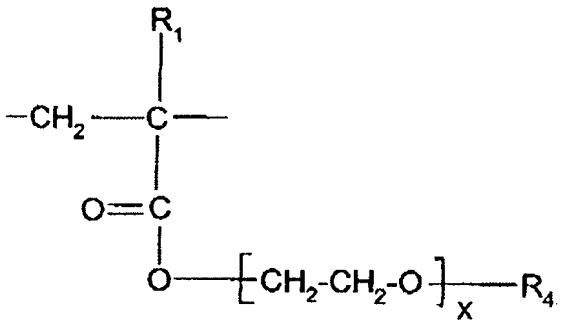
According to one particularly preferred form of the invention, the unit of formula (II) comprises at least one alkylene oxide unit ($x \geq 1$) and preferably a polyoxyalkylenated chain. The polyoxyalkylenated chain preferably consists of ethylene oxide units and/or of propylene oxide units and even more particularly consists of ethylene oxide units. The number of oxyalkylene units generally ranges from 3 to 100, more preferably from 3 to 50 and even more preferably from 7 to 25.

Among these polymers, mention may be made of:

- crosslinked or noncrosslinked, neutralized or non-neutralized copolymers comprising from 15% to 60% by weight of AMPS units and from 40% to 85% by weight of (C_8-C_{16})alkyl(meth)acrylamide units or of (C_8-C_{16})alkyl (meth)acrylate units, relative to the polymer, such as those described in patent application EP-A-750 899;
- terpolymers comprising from 10 mol% to 90 mol% of acrylamide units, from 0.1 mol% to 10 mol% of AMPS units and from 5 mol% to 80 mol% of n-(C_6-C_{18})alkylacrylamide units, such as those described in patent US-5 089 578.

Mention may also be made of non-crosslinked and crosslinked copolymers of partially or totally neutralized AMPS and of dodecyl methacrylate, and also non-crosslinked and crosslinked copolymers of partially or totally neutralized AMPS and of n-dodecylmethacrylamide, such as those described in the Morishima articles mentioned above.

Mention will be made more particularly of copolymers consisting of 2-acrylamido-2-methylpropanesulfonic (AMPS) acid units of formula (I) and of units of formula (III) below:



(III)

in which x denotes an integer ranging from 3 to 100, preferably from 5 to 80 and more preferably from 7 to 25; R_1 has the same meaning as that given above in formula (II) and R_4 denotes a linear or branched C_6-C_{22} and more preferably C_{10}-C_{22} alkyl.

The polymers that are particularly preferred are those for which, in the unit (III), x = 25, R_1 denotes methyl and R_4 represents C_{16}-C_{18} or C_{22}.

The preferred amphiphilic polymers in accordance with the invention may be obtained according to the standard free-radical polymerization processes in the presence of one or more initiators such as, for example, azobisisobutyronitrile (AIBN), azobisdimethylvaleronitrile, ABAH (2,2-azobis[2-amidinopropane] hydrochloride), organic peroxides such as dilauryl peroxide, benzoyl peroxide, tert-butyl hydroperoxide, etc., mineral peroxide compounds such as potassium persulfate or ammonium persulfate, or H_2O_2 optionally in the presence of reducing agents.

The amphiphilic polymers are obtained especially by free-radical polymerization in tert-butanol medium in which they precipitate.

Using precipitation polymerization in tert-butanol, it is possible to obtain a size distribution of the polymer particles that is particularly favourable for its uses.

The size distribution of the polymer particles may be determined, for example, by laser diffraction or image analysis.

An advantageous distribution for this type of polymer, determined by image analysis, is as follows: 60.2% less than 423 microns, 52.0% less than 212 microns, 26.6% less than 106 microns, 2.6% less than 45 microns and 26.6% greater than 850 microns.

The reaction may be performed at a temperature of between 0 and 150°C, preferably between 10 and 100°C, either at atmospheric pressure or under reduced pressure. It may also be performed under inert atmosphere, and preferably under nitrogen.

According to this process 2-acrylamido-2-methylpropanesulfonic acid (AMPS) or a sodium or ammonium salt thereof was especially polymerized with a (meth)acrylic acid ester and

- a C_{10}-C_{18} alcohol oxyethylenated with 8 mol of ethylene oxide (Genapol® C-080 from the company Hoechst/Clariant),
- a C_{11} oxo alcohol oxyethylenated with 8 mol of ethylene oxide (Genapol® UD-080 from the company Hoechst/Clariant),
- a C_{11} oxo alcohol oxyethylenated with 7 mol of ethylene oxide (Genapol® UD-070 from the company Hoechst/Clariant),
- a C_{12}-C_{14} alcohol oxyethylenated with 7 mol of ethylene oxide (Genapol® LA-070 from the company Hoechst/Clariant),
- a C_{12}-C_{14} alcohol oxyethylenated with 9 mol of ethylene oxide (Genapol® LA-090 from the company Hoechst/Clariant),
- a C_{12}-C_{14} alcohol oxyethylenated with 11 mol of ethylene oxide (Genapol® LA-110 from the company Hoechst/Clariant),
- a C_{16}-C_{18} alcohol oxyethylenated with 8 mol of ethylene oxide (Genapol® T-080 from

the company Hoechst/Clariant),

- a C_{16}-C_{18} alcohol oxyethylenated with 15 mol of ethylene oxide (Genapol® T-150 from the company Hoechst/Clariant),

- a C_{16}-C_{18} alcohol oxyethylenated with 11 mol of ethylene oxide (Genapol® T-110 from the company Hoechst/Clariant),

- a C_{16}-C_{18} alcohol oxyethylenated with 20 mol of ethylene oxide (Genapol® T-200 from the company Hoechst/Clariant),

- a C_{16}-C_{18} alcohol oxyethylenated with 25 mol of ethylene oxide (Genapol® T-250 from the company Hoechst/Clariant),

- a C_{18}-C_{22} alcohol oxyethylenated with 25 mol of ethylene oxide and/or a C_{16}-C_{18} iso alcohol oxyethylenated with 25 mol of ethylene oxide.

These AMPS copolymers and the process for preparing them have been described especially in French patent application 2 818 543.

The molar % concentration of the units of formula (II) and of the units of formula (III) in the polymers according to the invention will vary as a function of the desired cosmetic use and of the desired rheological properties of the formulation. It may range between 0.1 mol% and 99.9 mol%.

Preferably, for the most hydrophobic polymers, the molar proportion of units of formula (II) or (III) ranges from 50.1% to 99.9%, more particularly from 70% to 95% and even more particularly from 80% to 90%.

Preferably, for the sparingly hydrophobic polymers, the molar proportion of units of formula (II) or (III) ranges from 0.1% to 50%, more particularly from 5% to 25% and even more particularly from 10% to 20%.

The monomer distribution in the polymers of the invention may be, for

example, alternating, block (including multiblock) or random.

The viscosities (measured at 25°C using a Brookfield viscometer, needle No. 7) of the aqueous 1% solutions preferably range from 20 000 mPa.s to 100 000 mPa.s and more particularly from 60 000 mPa.s to 70 000 mPa.s.

The amphiphilic polymers in accordance with the invention are present in the oxidizing O/W emulsions in concentrations ranging from 0.01% to 10% by weight, more preferably from 0.01% to 5% and even more preferably from 0.01% to 2% by weight relative to the total weight of the emulsion.

Oxidizing agent

According to the invention, the oxidizing agent is preferably chosen from the group formed by hydrogen peroxide and compounds capable of producing hydrogen peroxide by hydrolysis, or mixtures thereof.

The oxidizing agent is preferably chosen from the group formed by aqueous hydrogen peroxide solution, urea peroxide, alkali metal bromates or ferricyanides and persalts such as perborates or persulfates, or mixtures thereof. One or more redox enzymes such as laccases, peroxidases and 2-electron oxidoreductases (such as uricase) may also be used as oxidizing agent, where appropriate in the presence of the respective donor or co-factor thereof.

More particularly, the oxidizing agent is hydrogen peroxide and especially aqueous hydrogen peroxide solution.

The hydrogen peroxide concentration may range from 0.15% to 12% and preferably from 0.6% to 9%, and the concentration of compound capable of forming hydrogen peroxide by hydrolysis may range from 0.1% to 25% by weight relative to the total weight of the oxidizing emulsion.

Preferably, when the oxidizing agent is aqueous hydrogen peroxide solution, the oxidizing emulsion according to the invention contains at least one hydrogen peroxide stabilizer, which may be chosen especially from alkali metal or alkaline-earth metal pyrophosphates, alkali metal or alkaline-earth metal stannates, phenacetin or salts of acids and of oxyquinoline, for instance oxyquinoline sulfate. Advantageously, at least one stannate optionally in combination with at least one pyrophosphate is used.

It is also possible to use salicylic acid and its salts, pyridinedicarboxylic acid and its salts, paracetamol and systems consisting of a) a buffer [ammonium or alkali metal (Na or K) borate and preferably sodium tetraborate decahydrate], b) an alkaline agent (NH_4OH, monoethanolamine, ammonium carbonate, ammonium hydrogen carbonate or sodium hydroxide), and c) an agent for sequestering ions of heavy metals (Fe, Mn or Cu) such as those described in patent applications WO 01/72271, WO 01/72272 and WO 01/52801.

In the oxidizing emulsions according to the invention, the concentration of hydrogen peroxide stabilizers may range from 0.0001% to 5% by weight and preferably from 0.01% to 2% by weight relative to the total weight of the oxidizing emulsions.

In the oxidizing emulsions according to the invention containing aqueous hydrogen peroxide solution, the concentration ratio of the hydrogen peroxide to the stabilizers may range from 0.05 to 1 000, preferably from 0.1 to 500 and even more preferably from 1 to 200. Similarly, the concentration ratio of the amphiphilic polymer(s) according to the invention to the stabilizers may range from 0.05 to 1 000, preferably from 0.1 to 500 and even more preferably from 1 to 200.

Preferably, according to the invention, the concentration ratio of the

amphiphilic polymer(s) according to the invention to the oxidizing agents is between 0.001 and 10, the amounts of the said polymers and oxidizing agents being expressed as active materials (hydrogen peroxide for the aqueous hydrogen peroxide solution). Even more preferably, this ratio is between 0.01 and 5 and even more particularly between 0.02 and 1.

C_8-C_{30} fatty alcohols

According to the invention, the term "fatty alcohol" means any pure, saturated or unsaturated, linear or branched fatty alcohol.

Among these fatty alcohols, C_{12}-C_{22} fatty alcohols are preferred.

Mention may be made among these of lauryl alcohol, cetyl alcohol, stearyl alcohol, oleyl alcohol, behenyl alcohol, linoleyl alcohol, undecylenyl alcohol, palmitoleyl alcohol, linolenyl alcohol, arachidonyl alcohol and erucyl alcohol, and mixtures thereof.

Cetyl alcohol is more particularly preferred.

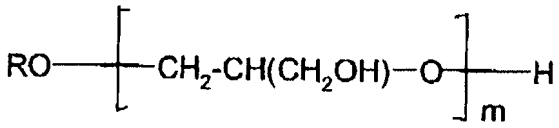
In the oxidizing emulsions according to the invention, the fatty alcohol concentration may range from about 0.1% to 30% by weight and more preferably from about 0.5% to 15% by weight relative to the total weight of the emulsion.

Nonionic and/or anionic surfactants

The nonionic surfactants are compounds that are well known per se (see especially in this regard "Handbook of Surfactants" by M.R. Porter, published by Blackie & Son (Glasgow and London), 1991, pp. 116-178) and, in the context of the present invention, their nature is not a critical factor. Thus, they may be chosen especially (non-limiting list) from polyethoxylated and polypropoxylated alcohols, α-diols and alkylphenols, with a fatty chain containing, for example, 8 to 18 carbon atoms, the number of ethylene oxide or propylene oxide groups possibly ranging especially from 2

to 50. Mention may also be made of copolymers of ethylene oxide and of propylene oxide, condensates of ethylene oxide and of propylene oxide with fatty alcohols; polyethoxylated fatty amides preferably containing from 2 to 30 mol of ethylene oxide, polyglycerolated fatty amides containing on average 1 to 5 and in particular 1.5 to 4 glycerol groups; glycerolated fatty alcohols; oxyethylenated fatty acid esters of sorbitan containing from 2 to 30 mol of ethylene oxide; fatty acid esters of sucrose; fatty acid esters of polyethylene glycol, alkylpolyglycosides, N-alkylglucamine derivatives, and amine oxides such as (C_{10}-C_{14})alkylamine oxides or N-acylaminopropylmorpholine oxides.

According to the invention, among the nonionic surfactants that are preferably used are glycerolated fatty alcohols. Glycerolated fatty alcohols especially have the following structure:



(IV)

in which:

R represents a saturated or unsaturated, linear or branched radical containing from 8 to 40 carbon atoms and preferably from 10 to 30 carbon atoms;

m represents a number ranging from 1 to 30 and preferably from 1 to 10.

Compounds of this type that may be mentioned include lauryl alcohol containing 4 mol of glycerol (INCI name: Polyglyceryl-4 lauryl ether), lauryl alcohol containing 1.5 mol of glycerol, oleyl alcohol containing 4 mol of glycerol (INCI name: Polyglyceryl-4 oleyl ether), oleyl alcohol containing 2 mol of glycerol (INCI name: Polyglyceryl-2 oleyl ether), cetearyl alcohol containing 2 mol of glycerol, cetearyl alcohol

containing 6 mol of glycerol, oleocetyl alcohol containing 6 mol of glycerol and octadecanol containing 6 mol of glycerol.

The fatty alcohol may represent a mixture of fatty alcohols in the same respect that the value of m represents a random value, which means that, in a commercial product, several species of polyglycerolated fatty alcohols may coexist in the form of a mixture.

The anionic surfactants that may be used, alone or as mixtures, in the context of the present invention, are especially (non-limiting list) salts (in particular alkali metal salts and especially sodium salts, ammonium salts, amine salts, amino alcohol salts or magnesium salts) of the following compounds: alkyl sulfates, alkyl ether sulfates, alkylamido ether sulfates, alkylarylpolyether sulfates and monoglyceride sulfates; alkyl sulfonates, alkyl phosphates, alkylamide sulfonates, alkylaryl sulfonates, α-olefin sulfonates and paraffin sulfonates; (C_6-C_{24})alkyl sulfosuccinates, (C_6-C_{24})alkyl ether sulfosuccinates and (C_6-C_{24})alkylamide sulfosuccinates; (C_6-C_{24})alkyl sulfoacetates; (C_6-C_{24})acyl sarcosinates and (C_6-C_{24})acyl glutamates. It is also possible to use (C_6-C_{24})alkylpolyglycoside carboxylic esters such as alkylglucoside citrates, alkylpolyglycoside tartrates and alkylpolyglycoside sulfosuccinates, alkyl sulfosuccinamates; acyl isethionates and N-acyl taurates, the alkyl or acyl radical of all these various compounds preferably containing from 12 to 20 carbon atoms, and the aryl radical preferably denoting a phenyl or benzyl group. Among the anionic surfactants that may also be used, mention may also be made of fatty acid salts such as oleic, ricinoleic, palmitic and stearic acid salts, and coconut oil or hydrogenated coconut oil acids; acyl lactylates in which the acyl radical contains from 8 to 20 carbon atoms. It is also possible to use alkyl D-galactosideuronic acids and salts thereof,

polyoxyalkylenated (C_6-C_{24})alkyl ether carboxylic acids, polyoxyalkylenated (C_6-C_{24})alkylaryl ether carboxylic acids and polyoxyalkylenated (C_6-C_{24})alkylamido ether carboxylic acids and salts thereof, in particular those comprising from 2 to 50 alkylene oxide and in particular ethylene oxide groups, and mixtures thereof.

According to the invention, among the anionic surfactants that are preferably used are alkyl sulfates, alkyl ether sulfates and α-olefin sulfonates.

Mixtures of nonionic and anionic surfactants are more preferably used according to the invention.

The amounts of nonionic and/or anionic surfactants present in the emulsion according to the invention may range from about 0.1% to 30% and preferably from about 0.5% to 15% of the total weight of the emulsion.

The oxidizing O/W cream emulsions according to the invention have a pH preferably ranging from 1 to 6 and more preferably from 2 to 4.

The pH of these emulsions according to the invention may be obtained and/or adjusted conventionally by adding either basifying agents, for instance aqueous ammonia, monoethanolamine, diethanolamine, triethanolamine, isopropanolamine, 1,3-propanediamine, an ammonium or alkali metal carbonate or bicarbonate, an organic carbonate such as guanidine carbonate, or an alkali metal hydroxide, it being possible, obviously, for all these compounds to be taken alone or as a mixture, or acidifying agents, for instance hydrochloric acid, phosphoric acid, acetic acid, lactic acid, citric acid, tartaric acid and boric acid.

The O/W oxidizing cream emulsion may also comprise an effective amount of additives known for their use in oxidizing compositions for the oxidation dyeing of the hair or for bleaching and permanently reshaping the hair, such as

preserving agents, sequestering agents such as EDTA, DTPA and etidronic acid, antifoams, for instance simethicone, cationic and amphoteric substantive polymers, water-soluble thickening polymers, fragrances and dyes to colour the emulsion.

Needless to say, a person skilled in the art will take care to select the optional additional compound(s) mentioned above, such that the advantageous properties intrinsically associated with the emulsion according to the invention are not, or are not substantially, adversely affected by the envisaged addition(s).

Another subject of the invention is a process for the oxidation dyeing of human keratin fibres and in particular the hair, using a dye composition comprising, in a support that is suitable for dyeing the said fibres, at least one oxidation dye and an oxidizing emulsion as defined above.

According to this process, the said dye composition is applied to the fibres, the colour being revealed at acidic, neutral or alkaline pH with the aid of an oxidizing emulsion according to the invention that is applied simultaneously or sequentially, with or without intermediate rinsing. According to one particularly preferred embodiment of the dyeing process according to the invention, the dye composition is mixed, at the time of use, with an oxidizing emulsion according to the invention. The mixture obtained is then applied to the keratin fibres and is left in for 3 to 50 minutes approximately and preferably 5 to 30 minutes approximately, after which the fibres are rinsed, washed with shampoo, rinsed again and dried.

The oxidizing composition according to the invention may also be used in a process for bleaching human keratin fibres and in particular the hair.

The bleaching process according to the invention comprises a step of applying an oxidizing emulsion according to the invention to the keratin fibres, this

emulsion preferably comprising aqueous hydrogen peroxide solution in alkaline medium after extemporaneous mixing.

Conventionally, a second step of the bleaching process according to the invention is a step of rinsing the keratin fibres.

Another subject of the present invention is a process for permanently reshaping human keratin fibres and in particular the hair, using the oxidizing emulsion defined above as oxidizing composition.

According to this process, a reducing composition is applied to the keratin fibre to be treated, the keratin fibre being placed under mechanical tension before, during or after the said application, the fibre is optionally rinsed, the oxidizing emulsion of the present invention is applied to the optionally rinsed fibre, and the fibre is then optionally rinsed again.

The first step of this process consists in applying a reducing composition to the hair. This application is performed lock by lock or to the whole head of hair.

The reducing composition comprises at least one reducing agent, which may be chosen in particular from thioglycolic acid, cysteine, cysteamine, glyceryl thioglycolate, thiolactic acid, or salts of thiolactic acid or of thioglycolic acid.

The usual step of placing the hair under tension in a shape corresponding to the final shape desired for the hair (for example curls) may be performed by any means, especially a mechanical means, that is suitable and known per se for keeping the hair under tension, for instance rollers, curlers and the like.

The hair may also be shaped without the aid of external means, simply with the fingers.

Before performing the next optional rinsing step, it is conventionally

convenient to leave the head of hair, to which the reducing composition has been applied, at rest for a few minutes, generally between 5 minutes and one hour and preferably between 10 and 30 minutes, so to be sure to give the reducing agent the time to act correctly on the hair. This waiting phase preferably takes place at a temperature ranging from 35°C to 45°C, preferably while also protecting the hair with a hood.

In the second optional rinsing step, the hair impregnated with the reducing composition is rinsed thoroughly with an aqueous composition.

Next, in a third step, the oxidizing emulsion according to the present invention is applied to the hair thus rinsed, with the aim of fixing the new shape given to the hair.

As in the case of the application of the reducing composition, the head of hair to which the oxidizing emulsion has been applied is then conventionally left in a resting or waiting phase that lasts a few minutes, generally between 3 and 30 minutes and preferably between 5 and 15 minutes.

If the hair was maintained under tension by external means, these means (rollers, curlers and the like) may be removed from the hair before or after the fixing step.

Finally, in the last step of the process according to the invention, which is also an optional step, the hair impregnated with the oxidizing composition is rinsed thoroughly, generally with water.

The examples that follow illustrate the invention without being limiting in nature.

EXAMPLES

The two oxidizing compositions A and B below were prepared (amounts expressed in grams of Active Material (AM*)

	Composition A of the prior art	**Composition B** according to the invention
Cetyl alcohol	3	3
Sodium lauryl sulfate	0.5	0.5
Oleyl alcohol glycerolated with 2 mol of glycerol	0.45	0.45
Oleyl alcohol glycerolated with 4 mol of glycerol	0.35	0.35
Antifoam: Simethicone	0.045	0.045
Sequestering agent: DTPA	0.06	0.06
Tetrasodium pyrophosphate 10 H_2O...	0.02	0.02
Sodium stannate, 6 H_2O	0.04	0.04
Amphiphilic polymer according to the invention**		0.05
Aqueous 50% hydrogen peroxide solution	12 AM*	12 AM*
Aqueous 85% phosphoric acid solution ..... qs...pH..	3	3
Demineralized water....qs...	100	100

**Copolymer of AMPS (80)/C_{16}-C_{18} alkyl methacrylate oxyethylenated with 25 mol of ethylene oxide (20), crosslinked with TMPTA, prepared and described in French patent application 2 818 543.

The change in the texture/viscosity of the 2 compositions A and B were monitored for seven weeks.

To quantify the change in the texture over time, the parameter Δv has been defined.

Change in the texture over time: Δv = viscosity measured at time t - viscosity measured 24 hours after manufacture.

The viscosities were measured using a rheomat, at a temperature of 25°C and with a No. 2 spindle. They are expressed in deviation units.

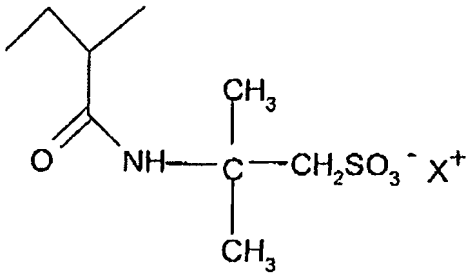
	Mean over 3 manufactures (1 measurement per manufacture) + standard deviation				
Time after manufacture	1 week	2 weeks	3 weeks	4 weeks	7 weeks
Δv (A)	5.0 (1.2)	10.0 (2.3)	15.0 (2.6)	18.0 (2.2)	-5.0 (2.1)
Δv (B)	2.6 (0.9)	2.6 (0.8)	4.6 (1.2)	6.0 (1.3)	7.0 (1.2)

These results demonstrate that composition B, in accordance with the invention, changes significantly less over time than the prior art composition A. In addition, it has been found that it shows better stability and will therefore maintain its use qualities better over time for use in dyeing, bleaching or permanently reshaping the hair.

After 7 weeks, composition B according to the invention also remains stable with respect to the aqueous hydrogen peroxide solution.

CLAIMS

1. Oxidizing cream oil-in-water emulsion for treating keratin materials, characterized in that it comprises at least one oxidizing agent, at least one (C_8-C_{30}) fatty alcohol, at least one nonionic and/or anionic surfactant and at least one amphiphilic polymer comprising at least one 2-acrylamido-2-methylpropanesulfonic acid unit in free form or partially or totally neutralized form of formula (I) below and at least one hydrophobic unit containing from 6 to 50 carbon atoms,



(I)

in which X^+ is a proton, an alkali metal cation, an alkaline-earth metal cation or an ammonium ion.

2. Emulsion according to Claim 1, characterized in that the hydrophobic unit of the amphiphilic polymer contains from 12 to 22 carbon atoms.

3. Emulsion according to either of the preceding claims, characterized in that the amphiphilic polymers have a number-average molecular weight ranging from 1 000 to 20 000 000 g/mol, preferably from 20 000 to 5 000 000 g/mol and more particularly from 100 000 to 1 500 000 g/mol.

4. Emulsion according to any one of the preceding claims, characterized in that an aqueous 1% by weight solution of the said polymers has, at a temperature of 25°C, a viscosity measured using a Brookfield viscometer, No. 7 needle, ranging from 20 000 mPa.s to 100 000 mPa.s.

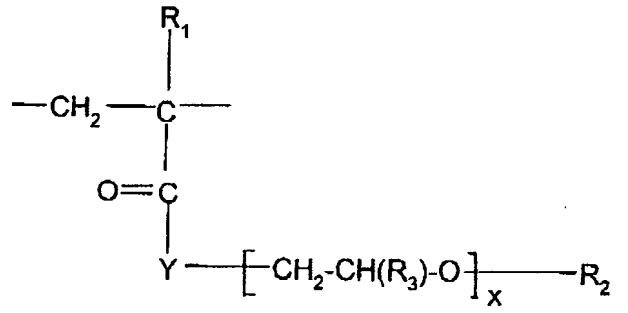
5. Emulsion according to any one of the preceding claims, characterized in that the amphiphilic polymers are prepared by free-radical polymerization by precipitation in tert-butanol.

6. Emulsion according to any one of the preceding claims, characterized in that the amphiphilic polymers are crosslinked or non-crosslinked, but preferably crosslinked.

7. Emulsion according to Claim 6, characterized in that the crosslinking agent(s) is(are) chosen from polyolefinically unsaturated compounds.

8. Emulsion according to Claim 7, characterized in that the crosslinking agent(s) is(are) chosen from methylenebisacrylamide, allyl methacrylate and trimethylolpropane triacrylate (TMPTA).

9. Emulsion according to any one of the preceding claims, characterized in that the hydrophobic unit is chosen from acrylates and acrylamides of formula (II) below:



(II)

in which R_1 and R_3, which may be identical or different, denote a hydrogen atom or a linear or branched C_1-C_6 alkyl radical (preferably methyl); Y denotes O or NH; R_2 denotes a hydrophobic hydrocarbon-based radical containing from 6 to 50 carbon atoms and more preferably from 12 to 22 carbon atoms; x denotes a number of moles of alkylene oxide and ranges from 0 to 100.

10. Emulsion according to Claim 9, characterized in that the hydrophobic radical R_2 is chosen from linear, branched or cyclic C_6-C_{18} alkyl radicals; C_6-C_{18} perfluoroalkyl radicals; the cholesteryl radical or a cholesterol ester; aromatic polycyclic groups.

11. Emulsion according to either of Claims 9 and 10, characterized in that the unit of formula (II) also comprises at least one alkylene oxide unit ($x \geq 1$).

12. Emulsion according to any one of Claims 9 to 11, characterized in that the unit of formula (II) also comprises at least one polyoxyalkylenated chain.

13. Emulsion according to Claim 12, characterized in that the polyoxyalkylenated chain consists of ethylene oxide units and/or of propylene oxide units.

14. Emulsion according to Claim 13, characterized in that the polyoxyalkylenated chain consists solely of ethylene oxide units.

15. Emulsion according to any one of Claims 9 to 14, characterized in that the number of oxyalkylene units ranges from 3 to 100, preferably from 3 to 50 and more particularly from 7 to 25.

16. Emulsion according to either of Claims 9 and 10, characterized in that the amphiphilic AMPS polymer is chosen from:

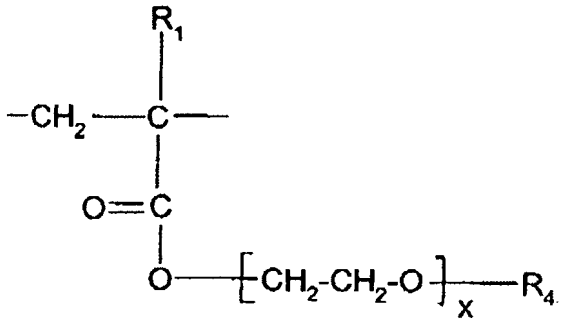
- crosslinked or noncrosslinked, neutralized or non-neutralized copolymers comprising from 15% to 60% by weight of AMPS units and from 40% to 85% by weight of (C_8-C_{16})alkyl(meth)acrylamide units or of (C_8-C_{16})alkyl (meth)acrylate units, relative to the polymer;
- terpolymers comprising from 10 mol% to 90 mol% of acrylamide units, from 0.1 mol% to 10 mol% of AMPS units and from 5 mol% to 80 mol% of n-(C_6-C_{18})alkylacrylamide

units, relative to the polymer.

17. Emulsion according to either of Claims 9 and 10, characterized in that the amphiphilic AMPS polymer is chosen from:

- non-crosslinked and crosslinked copolymers of partially or totally neutralized AMPS and of n-dodecyl methacrylate;
- non-crosslinked and crosslinked copolymers of partially or totally neutralized AMPS and of n-dodecylmethacrylamide.

18. Emulsion according to any one of Claims 9 to 15, characterized in that the amphiphilic AMPS polymer is chosen from copolymers consisting of 2-acrylamido-2-methylpropanesulfonic (AMPS) acid units of formula (I) and of units of formula (III) below:



(III)

in which x denotes an integer ranging from 3 to 100, preferably from 5 to 80 and more preferably from 7 to 25; R_1 has the same meaning as that given above in formula (II) and R_4 denotes a linear or branched C_6-C_{22} and more preferably C_{10}-C_{22} alkyl.

19. Emulsion according to Claim 18, characterized in that x = 25, R_1 is methyl and R_4 is C_{16}-C_{18} or C_{22}.

20. Emulsion according to Claim 9 or 18, characterized in that the molar percentage proportion of the units of formula (II) or of the units of formula (III) in the

polymers ranges from 50.1% to 99.9%.

21. Emulsion according to Claim 9 or 18, characterized in that the molar percentage proportion of the units of formula (II) or of the units of formula (III) in the polymers ranges from 0.1% to 50%.

22. Emulsion according to any one of the preceding claims, characterized in that the amphiphilic polymers are present in concentrations ranging from 0.01% to 10% by weight, more preferably from 0.01% to 5% by weight and even more preferably from 0.01% to 2% by weight, relative to the total weight of the emulsion.

23. Emulsion according to any one of the preceding claims, characterized in that the oxidizing agent is chosen from hydrogen peroxide, urea peroxide, alkali metal bromates or ferricyanides, persalts or mixtures thereof, redox enzymes such as laccases, peroxidases and 2-electron oxidoreductases, where appropriate in the presence of the respective donor or co-factor thereof.

24. Emulsion according to any one of the preceding claims, characterized in that the oxidizing agent is hydrogen peroxide.

25. Emulsion according to Claim 24, characterized in that the hydrogen peroxide concentration ranges from 0.15% to 12% and preferably from 0.6% to 9% by weight relative to the total weight of the emulsion.

26. Emulsion according to Claim 24, characterized in that the oxidizing agent is aqueous hydrogen peroxide solution.

27. Emulsion according to any one of the preceding claims, characterized in that the oxidizing agent concentration ranges from 0.1% to 25% by weight relative to the total weight of the emulsion.

28. Emulsion according to any one of the preceding claims, characterized in

that its pH ranges from 1 to 6 and preferably from 2 to 4.

29. Emulsion according to any one of the preceding claims, characterized in that the fatty alcohol(s) is(are) C_{12}-C_{22}.

30. Emulsion according to Claim 29, characterized in that the fatty alcohol is cetyl alcohol.

31. Emulsion according to any one of the preceding claims, characterized in that the fatty alcohol(s) is(are) present in concentrations ranging from 0.1% to 30% by weight and more preferably from 0.5% to 15% by weight relative to the total weight of the emulsion.

32. Emulsion according to any one of the preceding claims, characterized in that the anionic surfactant(s) is(are) chosen from alkyl sulfates, alkyl ether sulfates and α-olefin sulfonates.

33. Emulsion according to any one of Claims 1 to 31, characterized in that the nonionic surfactant(s) is(are) chosen from glycerolated fatty alcohols.

34. Emulsion according to any one of the preceding claims, characterized in that the surfactant(s) is(are) chosen from mixtures of nonionic and anionic surfactants.

35. Emulsion according to any one of the preceding claims, characterized in that the surfactant(s) is(are) present in concentrations ranging from 0.1% to 30% by weight and more preferably from 0.5% to 15% by weight relative to the total weight of the emulsion.

36. Process for the oxidation dyeing of human keratin fibres and in particular the hair using a dye composition comprising, in a support that is suitable for dyeing keratin fibres, at least one oxidation dye and an oxidizing emulsion as defined in any one of Claims 1 to 35.

37. Dyeing process according to Claim 36, according to which the dye composition is mixed, at the time of use, with the oxidizing emulsion; the mixture obtained is then applied to the keratin fibres and it is left in for 3 to 50 minutes approximately and preferably 5 to 30 minutes approximately, after which the fibres are rinsed, washed with shampoo, rinsed again and dried.

38. Dyeing process according to Claim 36, according to which the dye composition and the oxidizing emulsion are applied sequentially, with or without intermediate rinsing.

39. Process for treating human keratin fibres and in particular the hair in order to permanently reshape these fibres, in particular in the form of permanent-waved hair, this process comprising the following steps: (i) a reducing composition is applied to the keratin material to be treated, the keratin fibre being placed under mechanical tension before, during or after the said application, (ii) the keratin fibre is optionally rinsed, (iii) an oxidizing emulsion as defined in one of Claims 1 to 35 is applied to the optionally rinsed keratin fibre, (iv) the keratin fibre is optionally rinsed again.

40. Process for bleaching human keratin fibres and in particular the hair, comprising the following steps: i) an oxidizing emulsion according to any one of Claims 1 to 35 is applied to the keratin fibre, ii) the keratin fibre thus treated is rinsed.

41. Use of an amphiphilic polymer as defined in any one of Claims 1 to 21, to stabilize the viscosity of an oxidizing oil-in-water emulsion comprising at least one fatty alcohol and at least one nonionic and/or anionic surfactant.

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DESIGNATION OF THE INVENTOR(S) Page No. . 1 . / . 1
(if the applicant is not the inventor or the sole inventor)

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Your file references *(optional)*		OA02334/BN/FA	
NATIONAL REGISTRATION NO.		02/13,240	
TITLE OF THE INVENTION (200 characters or spaces maximum)			
Oil-in-water oxidizing cream emulsion for treating human keratin fibres			
THE APPLICANT(S):			
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DESIGNATE(S) AS INVENTOR(S): (Indicate top right "Page 1/1". If there are more than 3 inventors, use an identical form and number each page, indicating the total number of pages.)			
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DATE AND SIGNATURE(S) OF THE APPLICANT(S) OR OF THE REPRESENTATIVE (Name and capacity of the signatory) 23 October 2002 [signature] Catherine WATTREMEZ			